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(54) PROTECTION FILM FOR ELECTROLUMINESCENT ELEMENT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a protection film for an electroluminescent element with less performance drop caused by heat or stress, high gas barrier capability, and high transparency by forming a diamond-like carbon film having the specified hydrogen content and oxygen content on at least one side of a transparent film.
SOLUTION: A diamond-like carbon film having a hydrogen content of 50 atomic percent or less, preferably 45 atomic percent or less, more preferably 40 atomic percent or less and an oxygen content of 2-20 atomic percent, preferably 2-15 atomic percent, more preferably 2-10 atomic percent is formed on at least one side of a transparent film. As the transparent film, a film such as polyethylene terephthalate having not so high glass transition temperature, a light transmission of 85% or more, smooth surface, and a thickness of 0.01-1 mm is preferable. The diamond-like carbon film is prepared by using a raw material gas containing methane, carbon monoxide, or the like and by plasma CVD, and preferable to have a thickness of about 0.5 μm or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the bright film used for protection of electroluminescence.
[0002]
[Description of the Prior Art]From the former, in order [, such as foodstuffs and medicine,] to carry out deterioration prevention, packing these with a gas barrier film is performed. In the field of electronics, an electroluminescent element is protected with a gas barrier film, and the reinforcement is attained. It is known that the life of the electroluminescence luminescent device which covers an electroluminescent element with a gas barrier film will be influenced by the oxygen permeability and moisture permeability of a gas barrier film.
It is important to improve GASUBARIA nature and to aim at reduction of oxygen or the amount of water vapor permeation.

[0003]What provided the inorganic compound on the polyethylene terephthalate film, the polypropylene film, and the polyamide film as a gas barrier film is known. As the example, the film (JP,53-12953,B, JP,62-49856,B) which vapor-deposited oxidized silicon and an aluminum oxide can be mentioned to a film surface. However, when packing and covering various articles with a gas barrier film, although heat sealing is adopted, heat and stress will usually act on a film with a thing natural in that case. And when these gas barrier films were used, it was extended on the film with this heat and stress, the phenomenon arose, and an inorganic compound layer could not be followed in footsteps of this elongation phenomenon, but the very small crack occurred, and there was a problem that GASUBARIA nature will fall.
[0004]Therefore, although the gas barrier film which the inorganic compound layer which has GASUBARIA nature is provided at least in one side of a bright film, and grows into JP,4-139233,A was indicated, glass transition temperature needed to use a not less than 140 ** specific film. Transparency is bad although JP,6-344495,A has the indication of the gas barrier film used for protection of an electroluminescent element.
[0005]
[Problem(s) to be Solved by the Invention]There is little degradation by the heat and stress which act at the time of use, and this invention provides the film excellent in the transparency which can fully demonstrate GASUBARIA nature, also when not using a film with a high glass transition temperature as a substrate.
[0006]
[Means for Solving the Problem]In order that this invention person may solve the above-mentioned problem which conventional technology has, also when a general-purpose film is variously used as a result of research, even if heat and stress act, he finds out that a gas barrier film with producing [little] degradation is obtained, and came to complete this invention. That is, a gas barrier film concerning this invention forms at least in one side of a bright film a diamond-like-carbon film whose hydrogen concentration is below 50 atom % and whose oxygen density is 2-20atom%.
[0007]
[Embodiment of the Invention]The diamond-like-carbon film as used in the field of this invention is amorphous diamond like carbon, and each ingredient of a diamond, graphite,

and polymer is included. This diamond-like-carbon film differs [rate / which these ingredients mix] in character, and even if it is a diamond-like-carbon film which has high hardness, it does not necessarily work as gas barrier layers, such as a steam and oxygen.
[0008]Conventionally, the membraneous quality of a diamond-like-carbon film has been considered considering the hydrogen concentration as an index. That is, if hydrogen concentration becomes low, a film presents the character of a diamond more, on the other hand, if hydrogen concentration becomes high, the character of graphite or polymer will be presented and membranous hardness will fall. however, gas-barrier ** of a diamond-like-carbon film -- it is thought that there is necessarily nothing in membranous hardness and correspondence relations. Since it is thought that it is decided by concentration of the site where relation of the atoms which constitute gas-barrier ** and a film goes out, it has been thought that reduction of hydrogen concentration contributes to improvement in GASUBARIA nature.
[0009]In order that this invention person might improve membranous GASUBARIA nature, reduction of the hydrogen atom content in a film had been considered, but the transparency of the film obtained was not necessarily preferred. Then, the place which examined the method for raising the transparency of this film without making the hydrogen concentration in a film increase, It turned out that the effect of raising transparency is acquired, without worsening membranous GASUBARIA nature by making the oxygen atom considered to be a factor which worsens GASUBARIA nature in the former to a surprising thing contain moderately in a film. That is, the hydrogen concentration contained in the diamond-like-carbon film which works as barrier layers, such as a steam of this invention and oxygen, is below 50 atom %, and below 45 atom % is below 40 atom % still more preferably preferably. An oxygen density is 2-20atom% and is 2-10atom% preferably [it is desirable and] to 2-15atom% and a pan.
[0010]In order to form the above-mentioned diamond-like-carbon film, the material gas containing carbon and hydrogen is used. As material gas containing carbon and hydrogen, for example Methane, ethane, Alkane system gas, such as propane, butane, pentane, and hexane; Ethylene, Alkene series gas, such as propylene, a butene, and a pentene, pentadiene, Alkadiene system gas, such as butadiene; Alkyne system gas; benzene, such as acetylene and methylacetylene, Aromatic hydrocarbon system gas, such as toluene, xylene, indene, naphthalene, and phenanthrene; Cyclopropane, Cycloalkene system gas, such as cyclohexane; aldehyde system gas, such as ketone system gas; methanal, such as alcohol system gas, such as methanol and ethanol, acetone, and methyl ethyl ketone, and ethanal, is mentioned. The above-mentioned gas may be used alone and two or more sorts may be used together.
[0011]As material gas containing carbon and hydrogen, As the above-mentioned material gas, the above-mentioned material gas and the mixture; carbon monoxide gas of hydrogen gas, The mixture of the gas which comprises only carbon, such as choke damp, and oxygen, and the above-mentioned gas; Carbon monoxide gas, The mixture of the gas and hydrogen gas which comprise only carbon, such as choke damp, and oxygen; a mixture with the gas, the oxygen gas, and the steam which comprise only carbon, such as carbon monoxide gas and choke damp, and oxygen, etc. are mentioned. As material gas containing carbon and hydrogen, the mixed gas of the above-mentioned material gas and rare gas is mentioned. For example, helium, argon, neon, a xenon, etc. may be mentioned, these may be used alone, and two or more sorts may be used together.

[0012]Hydrogen gas in the above-mentioned mixed gas and the mixed amount of rare gas change with kinds of device, kinds of mixed gas, forming pressure, etc. to be used. So that the hydrogen concentration specifically contained in the formed diamond-like-carbon film may become 50 atom %, Preferably, below in 45 atom %, it adjusts so that it may become 40% or less still more preferably, and moreover, 2 to 20%, an oxygen density adjusts so that it may become 2-10 atom % preferably [it is desirable and] to 2-15atom% and a pan. As a carbon source, it is usable and is used, also installing the solid of carbon isotopes, such as black lead and a diamond, into hydrogen gas or rare gas atmosphere plasma.
[0013]As a means to excite the above-mentioned material gas by plasma, For example, the method of carrying out plasma decomposition by the method; electron cyclotron resonance which impresses the method; high frequency which impresses and carries out plasma decomposition of the direct current, and carries out plasma decomposition by the method; microwave discharge which carries out plasma decomposition; the method of carrying out a pyrolysis with heating by a hot filament, etc. are mentioned. Since plasma does not occur when a substrate is a plastics film which is an insulating material, the method of impressing direct current plasma in these is not preferred. Since a filament must be made into not less than 500 ** and an elevated temperature when using a hot filament method, it may not be desirable if the heat resistance of a substrate is taken into consideration. Since membrane formation speed is quick and forming temperature is low, the method of decomposing plasma by the microwave plasma method or a electron cyclotron resonance is preferred. When forming membranes to the resin film of a large area, it is preferred to use a high frequency plasma process. As a method of forming a diamond-like-carbon film, there is physical vapor deposition, such as ion beam sputtering and the ion plating method, and these methods may be adopted.
[0014]Although the thickness of the above-mentioned diamond-like-carbon film is determined if needed, Since adhesion with a base film will worsen, a coating will change by membrane stress or transparency will worsen if it becomes thick, 0.5 micrometer or less is preferred and 0.05 micrometer or less is still more preferably preferred 0.1 micrometer or less more preferably.
[0015]As the above-mentioned plastics film base, For example, polyester film, such as polyethylene terephthalate; Polyethylene, Polyolefin film; polystyrene-films; polyamide film; polycarbonate film; polyacrylonitrile film; polyether imide; polyether sulphone; Pori Sall John, such as polypropylene and polybutene; it is usable in polyimide etc.
[0016]The light transmission of a base film is not less than 88% preferably [considering it as not less than 85%], and more preferably. An oriented film or an unstretched film may be sufficient as the above-mentioned plastic film base material, and 0.01-1 mm of thickness is preferred. The higher one in the ability to do of the smooth nature of a film surface is preferred. When surface smoothness is low, it is because there is a possibility that GASUBARIA nature may fall. 0.10 micrometer or less is desirable still more preferred, and, specifically, Rmax (maximum of the difference of a mountain and a valley) showing surface roughness is 0.05 micrometer or less. 10 nm or less of Ra showing the average of roughness height is 5 nm or less preferably.
[0017]In order to improve the adhesion of the above-mentioned plastics film base surface, necessity may be accepted and publicly known processing of the plasma treatment by activated gas, such as inactive gas, such as helium, and oxygen gas, etc. may

be carried out to cleaning processings, such as washing for degreasing this base material surface and drying, and a base material surface within a vacuum housing.
[0018]Below <the generation method of a diamond-like-carbon film> explains the device used for this invention, referring to drawings. Drawing 1 is a mimetic diagram showing one example of the device which generates the diamond-like-carbon film of this invention. In drawing 1, 1 is a vacuum housing and it is the base film which stuck 2 on the RF electrode and 3 stuck on the Si wafer. As for an RF generator and 6, 4 is [a cold plate and 8] gas introducing pipes a thermo couple and 7 a consistency machine and 5.
[0019]Although temperature control of the above-mentioned base film is performed by methods, such as a circuit system of a fluid or a gas, infrared rays, and energizing heating, its circuit system of the fluid with large calorific capacity in which it is preferred being held at least below at the glass transition point of a base film is preferred. Under the present circumstances, as a fluid to circulate, the fluid warmed or cooled is mentioned to a predetermined temperature, and as a fluid through which it circulates, water, ethylene glycol (antifreeze solution), alcohols, and when low-temperature-izing further, liquid nitrogen, liquid helium, etc. are used suitably.
[0020]In order to have extended enough the composition range of the material gas which can be used and to improve the membranous quality, it is preferred to impress DC bias to a substrate, as a DC bias value, -500 - 100V is preferred, and it is -400 - 10V more preferably.
[0021]Next, membrane formation operation is explained. First, let the inside of a vacuum housing be a high vacuum after installing the plastic film base material stuck on the Si wafer on the cold plate 7 in the vacuum housing 1. In order to lose the influence on membrane formation by remains of other impurity gas, below 10^{-4}Torr of the degree of vacuum at this time is preferred. Subsequently, material gas is introduced from a gas introducing pipe, and it maintains at a predetermined pressure. The pressure at this time has $1x10^{-3}$ - preferred 10Torr.
[0022]The gas barrier film concerning this invention may be a thing of the lamination type made to unify by the method of joining the specified number by adhesives etc. and thermal melting arrival, etc. Since the heat-sealing nature at the time of use is raised, hot melt adhesive can be provided. Although it is preferred for this adhesives layer to provide in a diamond-like-carbon membrane layer, it can also provide on a bright film. Hot melt adhesive can use a general-purpose thing, and can use what uses an ethylene-vinylacetate copolymer, polyethylene, polypropylene, etc. as the main ingredients.
[0023]
[Example]
(Example 1) After sticking a 50-micrometer-thick polyethylene terephthalate film (the "lumiler quantity transparent type" by Toray Industries, Inc.) on a Si wafer, it installed on the cold plate 7 in the vacuum housing 1 shown in drawing 1, and the inside of a vacuum housing was decompressed to $1x10^{-5}$Torr. Subsequently, gas is introduced from the introducing pipe 8. C_2H_2 is set as 50sccm. After setting the pressure of a reaction chamber to $10x10^{-3}$Torr, membrane formation was performed for 2 minutes by impressing the frequency of 13.56 MHz, and the high-frequency power of 150W.
[0024]The thickness of the film determined by observation of a transmission electron microscope was about 0.1 micrometer. As a result of Raman spectroscopy's estimating the obtained film, it was checked that it is a diamond-like-carbon film. pentatomic %

When the membranous presentation was determined using SIMS, 43atom% and oxygen were contained in the diamond-like-carbon film for hydrogen.
[0025](Example 2) To the 50-micrometer-thick polyethylene terephthalate film (the "lumiler" by Toray Industries, Inc.), membranes were formed by the same method as Example 1.
[0026](Example 3) To the 12-micrometer-thick polyethylene terephthalate film ("OPET" by TOH CELLO CO., LTD.), membranes were formed by the same method as Example 1.
[0027](Comparative example 1) To the 50-micrometer-thick polyethylene terephthalate film (the "lumiler quantity transparent type" by Toray Industries, Inc.), membranes were formed by the same method as Example 1.
[0028](Comparative example 2) To the 50-micrometer-thick polyethylene terephthalate film (the "lumiler" by Toray Industries, Inc.), membranes were formed by the same method as Example 1.
[0029](Comparative example 3) To the 12-micrometer-thick polyethylene terephthalate film ("OPET" by TOH CELLO CO., LTD.), membranes were formed by the same method as Example 1.
[0030]The film and base film which vapor-deposited the diamond-like-carbon film formed in the substrate in the <evaluation of diamond-like-carbon film> above-mentioned example and the comparative example with the following valuation method are evaluated, and the result is shown in Table 1.
(1) The gas permeability measuring device by moisture-vapor-transmission Mocon was used, and it measured on 40 ** and the conditions of 90% of relative humidity.
(2) The gas permeability measuring device by oxygen transmittance YANAKO was used, and it carried out by 23 ** oxygen environment.
(3) Light transmission, the degree (HAZE) of haze, b value (yellow and blue comparatively)
It measured using the integrating sphere type hazemeter (Nippon Denshoku ND-1001D).
[0031]
[Table 1]

表1

	ガスバリアー性		透明性		
	透湿度（g／m²／日）	酸素透過度（ｃｃ／m²／日）	光線透過率（%）	ＨＡＺＥ（%）	b値
実施例 1	2．9	0．1	83．2	1．1	5．9
2	3．0	0．1	82．4	6．8	6．8
3	2．0	0．1	83．1	3．6	5．4
比較例 1	11．6	28．8	89．6	1．1	0．9
2	12．0	39．8	88．3	7．0	2．2
3	62．6	131	88．8	2．9	0．9

[0032]The film produced on the same conditions as a <evaluation of flexibility> (example 4) example was crooked 100 times using the Gelboflex circuit tester, and excess, such as moisture vapor transmission and oxygen, was measured.
[0033](Comparative example 4) With the publicly known vacuum evaporator, about 0.1 micrometer of silicon oxide was formed under the oxygen environment of pressure 6x10-5Torr to the base material surface of the 12-micrometer-thick polyethylene terephthalate film (the "lumiler" by Toray Industries, Inc.), using SiO as an evaporation source. It was crooked 100 times using the Gelboflex circuit tester, and the moisture vapor transmission before and behind that and oxygen transmittance were measured.
[0034]
[Table 2]
表2

	透湿度（g／m²／日）	酸素透過度（ｃｃ／m²／日）
実施例４ 屈曲前	2．0	0．1
屈曲後	23．3	39．3
比較例４ 屈曲前	4．0	2．3
屈曲後	51．6	84．4

[0035]Polyester film (70 ** of <trial production of EL element> (example 5) glass transitions, the transmissivity of 88% of a beam of light with a wavelength of 550 nm, and 50 micrometers in thickness) (on one side by Toray Industries, Inc. "lumiler", the diamond-like-carbon film (DLC) was formed so that thickness might be set to 100 nm with plasma CVD method.) And these two deposition films were piled up so that it might

become the order of film DLC-film DLC, and uniting was carried out with transparent adhesives. Next, the lamination type gas barrier film was obtained by forming the hot melt adhesive which comprises an ethylene-vinylacetate copolymer (8 % of the weight of vinyl acetate contents) with a melting extrusion method on a DLC layer.
[0036]The transparent electrode which provides the transparent electrode layer which changes from the mixture of indium oxide and the tin oxide to one side of a polyethylene terephthalate film apart from this on the other hand, The electroluminescent element which laminated the luminous layer which distributed the fluorescent powder end of a zinc sulfide system in cyanoethylation cellulose, the insulating layer which distributed titanium oxide powder in cyanoethylation cellulose, and the transparent electrode made from aluminum in this order is prepared. And a gas barrier film above-mentioned lamination type is piled up on both sides of this element so that a hot melt adhesive layer may become inside, The electroluminescence equipment of the structure which carried out coating protection with the gas barrier film was obtained by carrying out heat pressing using a roll on condition of the temperature of 130 **, roll linear pressure 5 kg/cm, and tension 3kgf. It was 2000 hours, when continuous action of this electroluminescence equipment was carried out according to the power supply (100V and 400 Hz) and that luminosity half-life was measured.
[0037](Comparative example 5) With the glass transition temperature of 70 **, 88% of light transmission with a wavelength of 550 nm, It is made to be the same as that of Example 4 except using oxidized silicon as a gas barrier layer, using a 50-micrometer-thick polyethylene terephthalate film (the "lumiler" by Toray Industries, Inc.) as a substrate of a gas barrier film, Lamination type a gas barrier film and electroluminescence equipment were obtained. When carrying out the continuation operation of this electroluminescence equipment like the example, the partial melanism phenomenon of the light-emitting surface was produced by a part for permeated water in about 200 hours, and luminosity half-life was as short as 800 hours.
[0038]
[Effect of the Invention]This invention is constituted as mentioned above, and without using a special film as a substrate, also when a general-purpose bright film is used, there is little degradation by the heat and stress which act at the time of use, and it can fully demonstrate GASUBARIA nature.
[0039]